STRESSES IN BOROPHOSPHOSILICATE GLASS FILMS DURING THERMAL CYCLING

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ABSTRACT

Stresses in thin films of borophosphosilicate glass deposited by atmospheric pressure CVD were measured during thermal cycling. Films of two different doping concentrations were examined for their flow properties. Initial heating produces an increase in the tensile stress as a consequence of film densification. Further heating leads to a decrease in the stress level as a result of plastic flow in the film. The addition of boron to PSG increases the tendency of the films to undergo plastic flow at elevated temperatures. Constant temperature flow behavior between 500 °C and 700 °C was non-linear. The activation energy for plastic flow was found to be 150 kcal/mole (6.5 eV/particle).

INTRODUCTION

The progression of integrated circuit technology to finer geometries has imposed serious restrictions on the surface topology in multilayer interconnection schemes. As higher aspect ratios are developed in response to the constrained planar dimensions, the degree of step coverage obtained in non-planar technologies is no longer sufficient to ensure conductor integrity and reliability. A solution to this problem involves the use of SiO_2 doped with boron and phosphorus oxides (BPSG) as an insulating dielectric layer between the gate-level interconnect and the first level of metal. Control of the composition of this dielectric layer allows the film to undergo plastic flow at temperatures which are significantly lower than required for pure SiO_2. The ability of the oxide to flow at low temperatures is necessary so that dopants within the active device regions of the substrate do not become redistributed during the planarization process. The ideal result is a quasi-planar surface prior to the deposition of the first level of metal.

The ability of the dielectric film to flow depends upon the local surface tension geometry and the viscosity at the process temperature. The driving force for the flow is the reduction in surface energy. The plastic response of the film is determined by the viscosity, which is a bulk property of the glass. Since the viscosity is a strong function of boron and phosphorus oxide content, it is necessary to maintain strict control over the dopant concentrations.

The technique which is commonly used for process evaluation consists of a measurement of the change in the angle at a step after some predetermined time and temperature cycle. Although this method is useful for relative comparisons, it is a not an objective benchmark of film performance. For example, two different production facilities may have furnaces with markedly different characteristics. Furthermore the analysis does not obtain any fundamental material properties. A more useful comparative tool would yield values of the material flow properties independent of thermal cycle and surface geometry.

This paper describes the observation of stresses in BPSG films. The film stress was derived from the measurement of the elastic bending of a substrate by the application of an optical lever. The isothermal relaxation of the film stress was analyzed to obtain the material flow properties.

EXPERIMENTAL DESCRIPTION

Thin films of borophosphosilicate glass were deposited by atmospheric pressure chemical vapor deposition (CVD). Films of two different compositions were obtained from reactors built by Watkins-Johnson Co. (W-J) and Applied Materials Technology Inc. (AMT). Film deposition was carried out on Si substrates with a (100) orientation. Prior to measurement the films were stored in normal room atmosphere. The film stress was derived from the elastic bending of the substrate. The bending of the substrates was measured with an optical lever in-situ during thermal annealing treatments. The ambient environment during the annealing cycles was Ar at one atmosphere. The maximum heating rate during transients was ~ 1.5 °C/s.This technique and the equipment used have been previously described (1). The basic relation between the substrate bending and the film stress is (2):

$$\sigma = E_s t_s^2 K/6(1-\nu_s)t_f \tag{1}$$

where E_s is Young's modulus of the substrate, ν_s is Poisson's ratio of the substrate, t_s and t_f are the thicknesses of the substrate and film, and K is the substrate curvature. The sensitivity of the equipment used was $\Delta\sigma$ ~ 5 MPa.

Creep tests were performed at constant temperature. When the temperature of the substrate is fixed, the total strain in the film is approximately constant. This condition is a consequence of the relative thicknesses of the substrate and the film. The substrate essentially imposes the planar dimension at any particular temperature on the film. Changes of the substrate curvature under these conditions reflects a redistribution between elastic strain and plastic strain in the film. This type of experiment corresponds to the stress relaxation technique which is employed in the testing of bulk materials. The expression which relates the plastic strain rate of the film to the curvature relaxation rate is:

$$d\varepsilon_p/dt = -(dK/dt)(E_s t_s^2(1-\nu_f)/E_f t_f(1-\nu_s)) \tag{2}$$

where E_f and ν_f are Young's modulus and Poisson's ratio of the film. In applying this expression to the current results a value of 10^{11} Pa was assumed for the biaxial elastic modulus of the film. The modulus is actually a function of the doping concentration and the temperature. These effects were neglected in the current work.

Structural information about the films was obtained using a Nicolet Model 20DX FTIR Spectrometer and also from an ellipsometer. The samples were kept under low vacuum conditions between annealing cycles and structural characterization.

Compositional analysis was performed with wet-chemical, calorimetric techniques.

RESULTS AND DISCUSSION

Figure 1 shows the variation of the stress in a BPSG film during annealing cycles to 920 °C. This film, deposited in a Watkins-Johnson reactor, was found to have a doping concentration of 3.4% B and 4.8% P by weight. The film thickness was 1.0 μm. A second set of films which was deposited in an AMT reactor had a concentration of 2.4% B and 3.0% P. The films deposited in the AMT reactor had a thickness of 0.57 μm. The stress evolution of the AMT films was similar except that the as-deposited stress was compressive, and the peak tensile stress during the first heating at ~500 °C was nearly twice as large. Although the as-deposited stresses were of opposite sign, the films deposited in the W-J reactor had an higher tensile stress following the deposition than indicated in the figure. The tensile stress level in these films appeared to decrease with time spent sitting on the shelf. This long-term transition to a compressive state has been previously observed in PSG films and was attributed to absorption of moisture into the film (3). The general shape of the initial heating curve from room temperature to 920 °C agrees qualitatively with behavior previously observed in phosphosilicate glass (PSG) films (3,4). The rise in tensile stress level to intermediate temperatures has been attributed to film densification (3). The maximum value of stress achieved between the densification and flow regimes was higher for the AMT film, with a value of 340 MPa. This observation agrees with the previous correlation between film thickness and stress maximum as reported for PSG films (3). The decrease in the tensile stress above 500 °C indicates plastic flow in the film. A small but perceptible shoulder is evident in the stress behavior of both films during plastic flow. This shoulder has been reported for PSG films (4).

Although the specific shape of the flow response is a function of the heating rate, the BPSG films appear to flow more readily than films without boron. Also the W-J film with the higher impurity content appears to exhibit flow at lower temperatures than the AMT film. Further heating and cooling generally induces an elastic response from the film within the accuracy of the measurement. However, a minor inelastic deviation is observed near 700 °C upon heating for the second cycle. The position of this inelastic deviation coincides with the shoulder contained on the flow portion of the initial heating response. The cause of the shoulder or the inelastic deviation in the second cycle is not known.

Figure 2 shows the stress variation of the W-J films during a series of annealing cycles employed to examine the structural evolution via FTIR spectroscopy and

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ellipsometry. A set of films was heated to increasingly higher temperatures with one sample being removed for analysis after each cooling stage. Since the alternate cooling from and heating to the densification - flow envelope occurred elastically, the samples obtained at room temperature should be structurally representative of points along the main envelope.

Figure 3 shows the FTIR spectra for the samples that were generated from the annealing cycles indicated in Figure 2. As the annealing temperature is increased a continuous increase in the absorbance intensity at each resonant frequency is observed. This causes the B-O · P-O doublet near 1400 cm^{-1} to become resolved in the more extensively annealed samples. This increase in the resolution of the spectra may indicate that the local structure is becoming more homogeneous throughout the sample as the extent of annealing is increased. The other effect which is observed is a small but noticeable shift of the dominant Si-O peak to higher wavenumber with increased annealing. It should be noted that the changes which occur in the sample do not cease after the transition from densification to flow behavior. Instead, the progression in the structure observed in the FTIR spectra proceeds throughout the annealing sequence.

Figure 4 shows the index of refraction and film thickness as measured by ellipsometry for a sample subjected to the thermal cycling shown in Figure 2. The index of refraction decreases abruptly during the initial annealing sequences and then rises continuously throughout the subsequent heat treatment. A value slightly higher than the initial value was attained after the final anneal. Other samples actually showed a higher final value of 1.47. This transition is accompanied by a reduction by ~ 4% in the film thickness. Assuming a biaxial modulus of 10^{11} Pa for the film, the extent of increase in stress shown in Figure 2 after the third cycle to 425 °C corresponds to ~ 1.8% strain in the film during densification. This shrinkage compares quite favorably with the reduction in film thickness for the annealing temperature of 425 °C. Since an additional 2% strain occurs during the flow dominated regime, it seems that the observed behavior is actually a superposition of densification and flow.

Figure 5 shows the stresses in a sample of W-J BPSG during several isothermal annealing cycles. Isothermal changes in the stress as a function of time are shown at four different temperatures; two during densification and two during flow. A fifth cycle to 710 °C remained at a tensile stress of 20 MPa for more than two hours, with no evidence of relaxation. In fact, this threshold stress level was maintained for all samples which were measured up to 920 °C. Previous reports for PSG films indicated this type of behavior only for undoped SiO_2 films. The time dependent behavior as seen during densification has been analyzed assuming a sintering model based on viscous flow (3). This type of analysis requires a detailed understanding of the high temperature flow behavior. The analysis of the densification will be left to a future publication so that adequate attention can be focused on the high temperature flow.

The expression describing the flow behavior of a material is often written in the following phenomenological form:

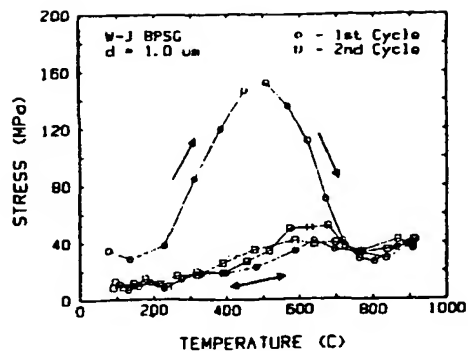$$d\epsilon_p/dt = C \sigma^n \tag{3}$$

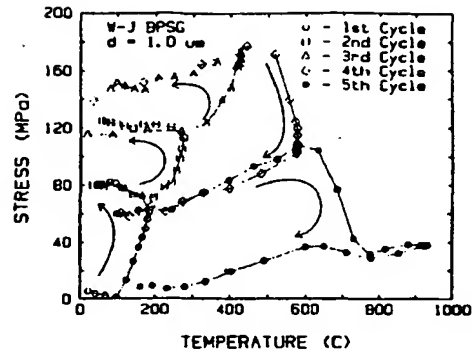Figure 1: Stress evolution of W-J BPSG. Dopant concentration was 3.4%B, 4.8% P.

Figure 2: Stress evolution of BPSG during thermal sequences which were used for FTIR analysis and ellipsometry.
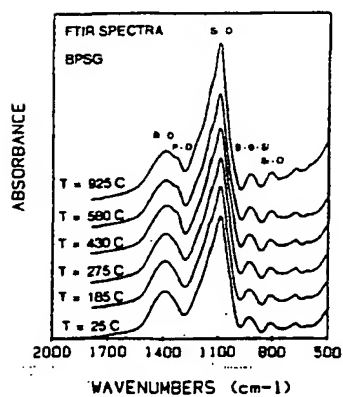
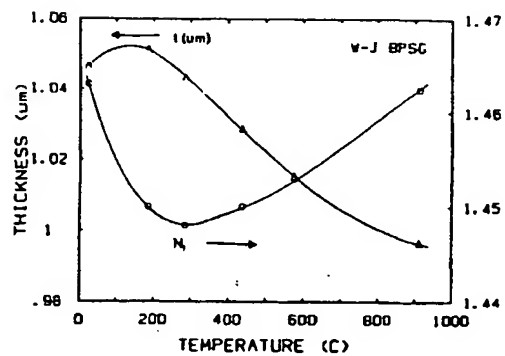Figure 3: FTIR spectra obtained for BPSG samples resulting from annealing cycles shown in Figure 2.

Figure 4: Film thickness and index of refraction for sample subjected to annealing cycles shown in Figure 2.
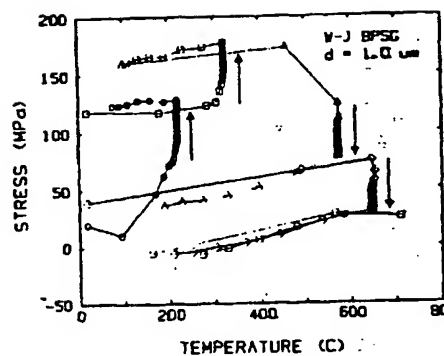
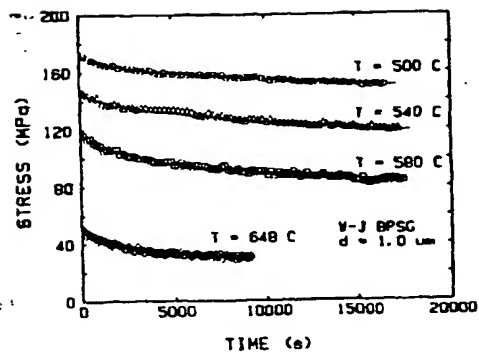Figure 5: Stress variation in BPSG films during isothermal annealing sequences.

Figure 6: Isothermal stress relaxation plots for W-J 'BPSG.
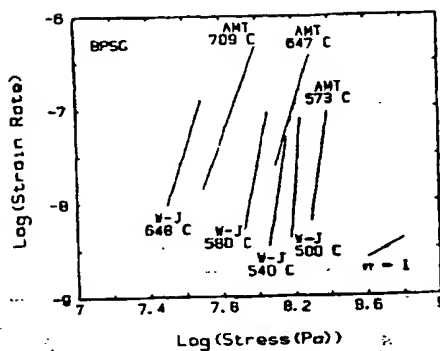
Figure 7: Strain rate vs. stress plot for two different concentrations of BPSG
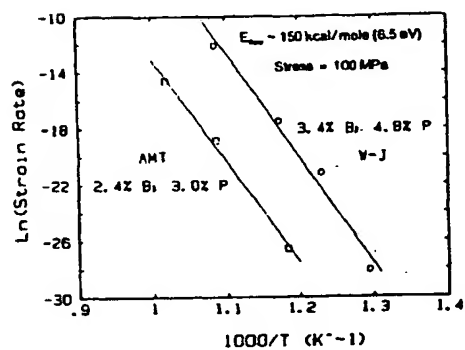
Figure 8: Arrhenius plot of constant stress flow rate.

where ε_p is the plastic strain, σ is the imposed stress, and n is the stress exponent, which takes on values greater than or equal to unity. Newtonian or linear flow is described by the case when n = 1. The proportionality constant, C, is thermally activated:

$$C = C_o \exp(-E_{flow}/kT) \tag{4}$$

In the characterization of glass behavior the parameter C is typically referred to as the fluidity. The reciprocal of C is the viscosity.

Figure 6 shows the stress relaxation curves of several BPSG films at four different temperatures. The flow parameters were obtained by differentiation of the data in Figure 6 to yield the plastic strain rate. Since the sensitivity of the experimental equipment is ~ 5 MPa, it was necessary to smooth the data in order to obtain reasonable values of the derivative.

Figure 7 shows a log-log plot of the plastic strain rate as a function of the stress for BPSG films of two different dopant concentrations. The slope for linear flow is shown for reference in the lower right hand corner. All of the measurements indicate non-linear flow in the range of stresses which were examined. The degree of non-linearity is most pronounced at the lower temperatures. Previous reports of non-linear flow in other silicate glass systems indicated ~ 10^8 Pa as a threshold limit between linear and non-linear flow(5). It was not possible to determine a threshold limit for the glass films in this study for two reasons. One problem is that the stress cannot be varied independently of the temperature. The second limitation is that the resolution of the equipment does not allow a precise evaluation of low strain rates. An interesting point to note is that the strain rate-stress characteristic for films of different composition at similar temperatures have nearly equivalent slopes.

Figure 8 shows an Arrhenius plot of the flow rates in Figure 7 at a constant stress of 10^8 Pa. The resulting slopes indicate an activation energy for flow of ~150 kcal/mole, or 6.5 eV/particle. This value compares quite favorably with values which have been obtained for flow in bulk silicate glasses(6). It further appears that the dopant concentration does not significantly affect the activation energy, but instead leads to markedly different values of the pre-exponential term.

This result is consistent with a model in which the same defect is responsible for the flow in both cases. The dopant level controls the concentration of the rate limiting defect. This leads to a strong interaction between the dopant concentration and the pre-exponential term, as observed. This correlation will have to be explored in greater detail before a more rigorous model can be developed.

CONCLUSIONS

Stresses in thin films of borophosphosilicate glass deposited by atmospheric pressure CVD were measured during thermal cycling. Films of two different doping concentrations

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were examined for their flow properties.

Initial heating to 500 °C produces an increase in the tensile stress as a consequence of film densification.

Further heating to 900 °C leads to a decrease in the stress level as a result of plastic flow in the film.

The general shape of the stress variation with temperature is similar to measurements of PSG films. The addition of boron oxide appears to increase the tendency of the films to undergo plastic flow at elevated temperatures.

Constant temperature flow behavior between 500 °C and 700 °C was non-linear. Further work is required to determine the dependence of the non-linearity on temperature.

The activation energy for plastic flow was found to be ~150 kcal/mole. This value compares favorably to data reported for flow in melts of bulk, silicate glasses. A simple model was suggested in which the B and P concentrations directly affect the pre-exponential factor of the material fluidity.

ACKNOWLEDGEMENTS

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MULTILEVEL METALLIZATION, INTERCONNECTION, AND CONTACT TECHNOLOGIES

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